

Filed November 9, 2001

In the United States Patent and Trademark Office

UTILITY PATENT APPLICATION

TITLE:

**ENHANCED STABILITY WATER-GAS SHIFT
REACTION CATALYSTS**

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ENHANCED STABILITY WATER-GAS SHIFT REACTION CATALYSTS

This application is a continuation-in-part of United States Patent Application Serial No. 09/771,812, filed January 29, 2001, which is a continuation-in-part of United States Patent Application Serial No. 09/669,044 filed September 25, 2000, now abandoned. The disclosures of both of these applications are incorporated herein by reference as if fully set forth herein.

The present invention relates to copper-based water gas shift catalysts comprising a stabilizing species that retards the deactivation rate of the catalysts during operational exposure to steam or water at low temperatures, such as below 220 °C. The present invention also relates to methods for the use of these catalysts for generating hydrogen by reaction of carbon monoxide (CO) and steam (gaseous H₂O), and in particular to generating hydrogen from a gas stream comprising hydrogen, water, and carbon monoxide. The catalysts and methods of the invention are useful, for example, in generating hydrogen in the gas stream supplied to fuel cells, particularly to proton exchange membrane (PEM) fuel cells.

Fuel cells directly convert chemical energy into electricity thereby eliminating the mechanical process steps that limit thermodynamic efficiency, and have been proposed as a power source for many applications. The fuel cell can be two to three times as efficient as the internal combustion engine with little, if any, emission of primary pollutants such as carbon monoxide, hydrocarbons and nitric oxides. Fuel cell-powered vehicles which reform hydrocarbons to power the fuel cell generate less carbon dioxide (green house gas) and have enhanced fuel efficiency.

Fuel cells, including PEM fuel cells [also called solid polymer electrolyte or (SPE) fuel cells], generate electrical power in a chemical reaction between a reducing agent (hydrogen) and an oxidizing agent (oxygen) which are fed to the fuel cells. A PEM fuel cell includes an anode and a cathode separated by a membrane which is usually an ion exchange resin membrane. The anode and cathode electrodes are typically constructed from finely divided carbon particles, catalytic particles supported on the carbon particles and proton conductive resin intermingled with the catalytic and carbon particles. In typical PEM fuel cell operation, hydrogen gas is electrolytically oxidized to hydrogen ions at the anode composed of platinum reaction catalysts deposited on a

conductive carbon electrode. The protons pass through the ion exchange resin membrane, which can be a fluoropolymer of sulfonic acid called a proton exchange membrane. H₂O is produced when protons then combine with oxygen that has been electrolytically reduced at the cathode. The electrons flow through an external circuit in this process to do work, creating an electrical potential across the electrodes. Examples of membrane electrode assemblies and fuel cells are described in US Pat. No. 5,272,017.

The water-gas shift reaction is a well known catalytic reaction which is used, among other things, to generate hydrogen in a gas-borne stream by chemical reaction of carbon monoxide with water vapor (H₂O) according to the following stoichiometry:



The reaction requires catalysts that are typically based on combinations of iron oxide with chromia for catalysis at high temperatures (about 350 °C), or mixtures of copper and zinc materials at lower temperatures (about 200 °C).

A problem encountered in water-gas shift processes using non-pyrophoric, copper-based water gas shift catalysts as disclosed in copending United States Patent Application Serial No. 09/771,812, filed January 29, 2001, is the decline in catalytic activity at lower temperatures in the presence of steam (H₂O). For example, at or below temperatures of about 220 °C, copper-based water-gas shift catalysts are deactivated by the presence of steam (H₂O). The problem of catalytic deactivation is of particular importance during startup and shutdown of water-gas shift reactors containing copper-based catalysts, wherein the temperature is dropped below the dew point of the input gas stream. Steam induced deactivation can also occur gradually, whereby the levels of unconverted carbon monoxide (CO) remaining downstream from the catalyst gradually rise with time. This gradual rise in downstream CO concentration while carrying out the water-gas shift reaction is indicative of a catalytic instability found in many different copper-based, low temperature water-gas shift catalysts that operate below 220 °C. In an industrial setting, where reaction conditions can be carefully monitored controlled, appropriate controls and protocols serve to prevent the deactivating effects of low temperature steam exposure. For example, the deactivation of certain copper-based water gas shift reaction catalysts can be reversed by oxidation under dry conditions, followed by reduction of the catalyst with dry hydrogen. These procedures, however, are

not easily implemented in a fuel processor that would be used in a vehicle, or in a residential setting.

Summary of the Invention

5 In one embodiment the invention relates to a catalyst having at least 50 wt.% of an oxide support on which is dispersed: at least 5 wt.% copper or an oxide thereof, 0.01 to 0.5 wt.% of a platinum group metal, and at least 10 wt.% of a reducible metal oxide. The oxide support is selected from the group consisting of activated alumina, zirconia, titania, silica, zeolites, and combinations thereof. In one preferred embodiment, the
10 oxide support is activated alumina. The platinum group metal is selected from platinum, palladium, rhodium, osmium, iridium, ruthenium and combinations thereof. In one preferred embodiment, the platinum group metal is platinum. The reducible metal oxide is selected from the group consisting of the oxides of chromium, vanadium, molybdenum, cerium, praseodymium, neodymium, titanium, nickel, manganese, cobalt
15 and combinations thereof. In a preferred embodiment, the reducible metal oxide is cerium oxide.

 In another embodiment, the invention relates to a catalyst having at least 50 wt.% of an alumina support; at least 5 wt.% copper or an oxide thereof dispersed on the alumina support; 0.01 to 0.5 wt.% of a platinum group metal, preferably platinum,
20 dispersed on the alumina support; and at least 10 wt.% cerium oxide dispersed on the alumina support. In a preferred aspect of this catalyst, there is at least 65 wt.% of the alumina support; 6 to 12 wt.% of copper or an oxide thereof, 0.01 to 0.5 wt.% of platinum, and 10 to 25 wt.% of cerium oxide dispersed on the alumina support.

 In one embodiment the catalyst is in the form of particles having a mesh size of
25 12 or greater, and a BET surface area of 10 m²/g or greater. In another embodiment, the catalyst is in the form of a washcoat composition deposited on a monolith substrate.

 In another aspect, the invention relates to a water-gas shift catalyst for converting carbon monoxide and steam into hydrogen and carbon dioxide. The water-gas shift catalyst has at least 50 wt.% of an alumina support, on which is dispersed at least 5 wt.%
30 copper or an oxide; 0.01 to 0.5 wt.% of a platinum group metal, preferably platinum, dispersed on the alumina support; and at least 10 wt.% cerium oxide dispersed on the alumina support.

In a preferred embodiment, there is at least 65 wt.% of the alumina support in the water-gas shift catalyst. Dispersed on the alumina support are 6 to 12 wt.% of copper or an oxide thereof; 0.01 to 0.5 wt.% of platinum, and 10 to 25 wt.% of cerium oxide. In a preferred embodiment, the alumina support is in the form of particles having a mesh size of 12 or greater, and a BET surface area of 10 m²/g or greater.

In another embodiment, the invention relates to a catalyst having a cerium oxide support, copper or an oxide thereof dispersed on the cerium oxide support, and 0.1 wt.% or more of a platinum group metal dispersed on the cerium oxide support. The platinum group metal is selected from the group consisting of platinum, palladium, rhodium, osmium, iridium, ruthenium and combinations thereof. A preferred platinum group metal is platinum. Preferably, there is 4 to 12 wt.% of copper or an oxide thereof dispersed on the cerium oxide support; and 0.1 wt.% to 2 wt.% platinum dispersed on the cerium oxide support. The catalyst is preferably in the form of a washcoat composition deposited on a monolith substrate.

In another aspect, the invention relates to a water-gas shift catalyst for converting carbon monoxide and steam into hydrogen and carbon dioxide. This water-gas shift catalyst has a cerium oxide support on which is dispersed copper or an oxide thereof and 0.1 wt.% or more of a platinum group metal, preferably platinum. In a preferred embodiment of the water-gas shift catalyst, there is 4 to 12 wt.% of copper or an oxide thereof, and 0.1 to 2 wt. % platinum dispersed on the cerium oxide support. Preferably the water-gas shift catalyst is in the form of a washcoat composition deposited on a monolith substrate.

The invention also relates to a process for producing hydrogen by contacting an input gas stream containing steam and carbon monoxide with a water-gas shift catalyst below 350 °C. The water-gas shift catalyst has at least 50 wt.% of an oxide support which can be activated alumina, zirconia, titania, silica, or zeolites; and is preferably activated alumina. Dispersed on the oxide support are copper or an oxide thereof, 0.01 to 0.5 wt.% of a platinum group metal, and a reducible metal oxide. The platinum group metal is platinum, palladium, rhodium, osmium, iridium, ruthenium and combinations thereof. In one preferred embodiment of the process, the platinum group metal is platinum. The reducible metal oxide selected from the group consisting of the oxides of

chromium, vanadium, molybdenum, cerium, praseodymium, neodymium, titanium, nickel, manganese, cobalt. Preferably, the reducible metal oxide is cerium oxide.

In another embodiment, the invention relates to a process for producing hydrogen, by contacting an input gas stream containing steam and carbon monoxide with
5 a water-gas shift catalyst below 350 °C. The water-gas shift catalyst has at least 50 wt.% of an oxide support selected from the group consisting of activated alumina, zirconia, titania, silica, zeolites, zinc oxide and combinations thereof. Preferably the oxide support includes activated alumina. Dispersed on the oxide support are copper or an oxide thereof, 0.01 to 0.5 wt.% of a platinum group metal (preferably platinum), and
10 cerium oxide. In a preferred embodiment of the process, the water-gas shift catalyst contains 10 wt.% or more cerium oxide. In another preferred process, the water-gas shift catalyst is in the form of particles having a mesh size of 12 or greater, and a BET surface area of 10 m²/g or greater.

In one embodiment of this process, the input gas stream has 10% by volume or
15 more of hydrogen, in addition to carbon monoxide and steam. In another embodiment, there is 10% by volume or more of steam in the input gas stream. In yet another embodiment, the input gas stream contains up to 2% by volume oxygen, in addition to carbon monoxide and steam.

The invention also relates to a preferred process for producing hydrogen by
20 contacting an input gas stream containing steam and carbon monoxide with a water-gas shift catalyst below 300 °C. In this preferred process, the water-gas shift catalyst has at least 50 wt.% of an alumina support. Dispersed on the alumina support are 6 to 12 wt.% of copper or an oxide thereof, about 0.01 to 0.5 wt.% platinum, and 10 to 25 wt.% cerium oxide dispersed on the alumina support. Preferably, the alumina support of the
25 water-gas shift catalyst is in the form of particles having a mesh size of 12 or greater, and a BET surface area of 10 m²/g or greater.

In an additional process aspect, the invention relates to another process for producing hydrogen, by contacting an input gas stream containing steam and carbon monoxide with a water-gas shift catalyst below 450 °C. In this process, the water-gas
30 shift catalyst has a cerium oxide support on which is dispersed copper or an oxide thereof and 0.1 wt.% or more of a platinum group metal, preferably platinum. Preferably, the

concentration of the copper or oxide thereof in the water-gas shift catalyst is about 4 to 12 wt.%.

In one embodiment of the process using this cerium oxide-supported, copper-based catalyst, the input gas stream contains 10% by volume or more of hydrogen, in addition to carbon monoxide and steam. In another embodiment, there is 10% by volume or more of steam in the input gas stream. In yet another embodiment, the input gas stream further has up to 2% by volume oxygen, in addition to carbon monoxide and steam.

In another aspect, the invention relates to an apparatus for supplying hydrogen to a PEM fuel cell with a hydrocarbon reformer reactor, a selective carbon monoxide oxidation reactor and a water-gas shift reactor. The hydrocarbon reformer reactor is upstream and in train with the water-gas shift reactor, and the preferential oxidation catalyst is downstream and in train with the water-gas shift reactor.

In one embodiment of the apparatus, the water-gas shift reactor contains a water-gas shift catalyst that has at least 50 wt.% of an oxide support selected from the group consisting of activated alumina, zirconia, titania, silica, zeolites and combinations thereof. Dispersed on the oxide support are copper or an oxide thereof, 0.01 to 0.5 wt.% of a platinum group metal, and at least 10 wt.% of a reducible metal oxide. The reducible metal oxide is preferably selected from the group consisting of the oxides of chromium, vanadium, molybdenum, cerium, praseodymium, neodymium, titanium, nickel, manganese, cobalt and dispersed on the oxide support.

In another embodiment of the apparatus, the water-gas shift reactor contains a water-gas shift catalyst that has a cerium oxide support, on which is dispersed copper or an oxide thereof and 0.1 wt.% or more of a platinum group metal.

Brief Description of the Drawings

Figure 1 is a depiction of one embodiment of fuel processor unit for supplying hydrogen to a fuel cell.

Figure 2 is a graphic representation the a single repeating subunit of a temperature profile used to analyze the steam induced deactivation of various copper-based water-gas shift catalysts.

Figure 3 is a graphic representation of test results obtained for the steam induced deactivation of various copper-based water-gas shift catalysts.

Definitions

The definitions of certain terms used herein are as follows:

- "activated alumina" means a high BET surface area alumina, for example greater than
 5 $10 \text{ m}^2/\text{g}$, preferably greater than $150 \text{ m}^2/\text{g}$ having primarily one or more of gamma, theta and delta aluminas.
- "BET surface area" means the Brunauer, Emmett, Teller method for determining surface area by N_2 adsorption. Unless otherwise specifically stated, all references herein to the surface area refer to the BET surface area.
- 10 "Catalyst A" refers to a catalyst of the invention that includes a refractory inorganic oxide support (e.g., alumina), a copper catalytic agent, a reducible metal oxide (e.g., cerium oxide) and one or more platinum group metals.
- "Catalyst B" refers to a catalyst of the invention that includes a cerium oxide support, a copper catalytic agent and one or more platinum group metals.
- 15 "catalytically effective amount" means that the amount of material present is sufficient to affect the rate of reaction of the water gas shift reaction in the sample being treated.
- "cerium oxide" includes all oxides of cerium including ceria (CeO_2).
- "cerium oxide support" refers to a particulate support material wherein cerium oxide is present, preferably in at least a concentration of 50 wt.% of the total catalyst weight.
- 20 Other composite materials may be present along with the cerium oxide, including for example, other rare earth oxides (e.g., oxides of lanthanum, praseodymium, neodymium), zirconium oxide and gallium oxide.
- "copper-based catalyst" refers to a catalyst that includes a copper catalytic agent. While platinum group metals or oxides thereof may be included in the composition, their
 25 concentrations are less, preferably at least five times lower (on a weight basis) than the copper or an oxide thereof.
- "high heat capacity support" means support materials with a heat capacity that is approximately equal to or, preferably, greater than that of the reducible metal oxide in the catalyst.
- 30 "high surface area support" means support materials with a BET surface area that is approximately greater than $10 \text{ m}^2/\text{g}$, preferably greater than $150 \text{ m}^2/\text{g}$.

“incipient wetness impregnation” means the impregnation of the catalyst support with a volume of metal salt solution substantially equal to the pore volume of the support material.

5 “inlet temperature” shall mean the temperature of the hydrogen, water, and carbon monoxide stream, test gas, fluid sample or fluid stream being treated immediately prior to initial contact of the hydrogen stream, test gas, fluid sample or fluid stream with a catalyst composition.

10 “percent by volume” refers to the amount of a particular gas component of a gas stream, unless otherwise indicated, means the mole percent of the gas component of the gas stream as expressed as a volume percent.

15 “wt.%” or “percent by weight”, means weight percent based on the weight of an analyte as a percentage of the total catalyst weight, including the support and any material impregnated therein, including without limitation the copper catalytic agent and any metal oxide material impregnated therein. The calculation does not include the monolith substrate in embodiments where the catalyst is in the form of a washcoat composition deposited on a monolith substrate.

“input gas stream” means a gas stream prior to passing through a catalytic region or prior to initial contact with a catalyst composition.

20 “supports” or “catalyst support” refer to particulate materials that are part of the catalyst composition including inorganic oxides including oxide support selected from the group consisting of activated alumina, zirconia, titania, silica, zeolites and combinations thereof for Catalyst A. Cerium oxide serves as the support for Catalyst B.

25 “VHSV” means volume hourly space velocity; that is, the flow of a reactant gas in liter per hour per liter of catalyst volume at standard temperature and pressure. In embodiments of the invention that include a monolith substrate, the determination includes the volume of the monolith substrate.

“WHSV” means weight hourly space velocity; that is the flow of a reactant gas in liter per hour per kilogram of catalyst.

Detailed Description of the Invention

Applicants have found that addition of low concentrations of platinum group metals to copper-based catalysts can reduce or prevent the deactivation of the catalysts that would otherwise occur upon exposure to steam at temperatures of about 220 °C and lower. These conditions are prevalent during startup and shutdown of reactors incorporating copper-based water gas shift catalysts. Applicants have also found methods of producing the new catalysts, that include low concentrations of platinum group metals, that are more resistant to steam-deactivation at lower temperatures. In other embodiments, the invention provides methods for the use of the water gas shift reaction catalysts in high steam environments at low temperatures. In addition, the invention provides apparatus for supplying hydrogen to a fuel cell that incorporates the catalysts of the invention.

It has been found that the degradation in catalytic activity of copper-based catalysts that typically occurs upon exposure to steam at low temperatures, e.g., below 220 °C, can be abated, or in some cases prevented, by adding low concentrations of platinum group metals to the catalyst. As mentioned above, these lower temperatures are typically encountered during startup or shutdown of water-gas shift reactors.

While it will be apparent to those of ordinary skill in the art that certain platinum group metals can serve as effective water-gas shift catalytic agents themselves, their use in the instant invention is believed to serve primarily as a stabilizing species to the copper catalytic agents. Certain copper-based water-gas shift catalysts display a gradual decline in the rate of carbon monoxide conversion (and production of hydrogen) over time when exposed to high steam concentrations at lower temperatures, e.g., below 220 °C. The inclusion of low concentrations of one or more platinum group metals in the copper-based catalyst compositions, however, lowers the observed deactivation rate under these conditions. In other words, the catalysts of the invention display an enhanced stability upon exposure to high steam concentrations at low temperatures.

In addition, the utilization of a base metal, copper, in the catalysts of the invention offers significant cost advantages over certain conventional, platinum-based water-gas shift catalysts that utilize higher concentrations of platinum group metals as catalytic agents. Only low concentrations of platinum group metals in the catalysts of

the invention are necessary to provide the catalysts their enhanced stability to high steam, low temperature environments.

The catalysts of the invention of the invention can be employed to catalyze reactions. For example, the catalysts of the invention can be employed to oxidize
5 chemical feedstocks, e.g., feedstocks containing carbon monoxide. In other embodiments the catalysts serve as water-gas shift catalysts for generating hydrogen and carbon dioxide from carbon monoxide and steam.

The catalysts of the invention include a catalyst support, copper or an oxide thereof as a catalytic agent, and one or more platinum group metals. The catalyst can be
10 in any form, including tablets, extrudates, washcoat compositions deposited on monolith substrates and high-strength, high heat capacity particulate catalysts.

In one embodiment, the invention relates to a catalyst that includes a refractory inorganic oxide support (e.g., alumina), a copper catalytic agent, a reducible metal oxide (e.g., cerium oxide) and one or more platinum group metals. For economy of expression
15 this catalyst will be referred to herein as "Catalyst A".

In a second embodiment, the invention relates to a catalyst that has a cerium oxide support, a copper catalytic agent and one or more platinum group metals. Here again, for reasons of convenience, this catalyst will be referred to herein as "Catalyst B".

20 Catalyst A

Catalyst A contains a refractory inorganic oxide support (e.g., alumina). Dispersed on the support are a copper catalytic agent, a reducible metal oxide (e.g., cerium oxide) and one or more platinum group metals. The catalyst can be in any form including extrudates, tablets, washcoat compositions deposited on monolith substrates
25 and high-strength particulate catalysts. A preferred form of the catalyst is as high mechanical strength, high-heat capacity particulate catalysts.

Typically, there is at least 5 wt.% of copper in the catalyst composition for Catalyst A, to serve as a catalytic agent. Preferably, there is at least 6 to 12 wt.% of copper in the catalyst composition. The copper catalytic agent can be in the form of
30 copper (II) oxide (CuO), copper (I) oxide (Cu₂O) or as metallic copper depending on the conditions that the catalyst is exposed to. The copper is generally dispersed on the inorganic oxide support by contacting the support with a water-soluble or water-dispersible salt of copper for sufficient time to impregnate the support, followed by a

drying step. The support material containing the copper is then calcined, preferably at a temperature above about 400 °C.

The catalysts of the invention include a platinum group metal as a stabilizing agent, which is selected from the group consisting of platinum, palladium, rhodium, iridium and ruthenium. Preferably, the platinum group metal is platinum, palladium or rhodium, with platinum being particularly preferred. The platinum group metals are typically dispersed on the support by contacting the support with a water-soluble or water-dispersible salt of the platinum group metal for sufficient time to impregnate the support. Non-limiting examples of such platinum group metal salts include nitrates, acetates, $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$, palladium and rhodium nitrate. The supported platinum group metal is then calcined to fix it to the support as the metal or as an oxide. Preferably, the amount of the platinum group metal salts is chosen so that the final concentration of the platinum group metal on the support is about 0.01 wt.% to about 0.5 wt.%.

In embodiments of Catalyst A wherein the support is a high heat capacity support with high mechanical strength, the platinum group metal is preferably impregnated into the support using methods that lead to a substantially uniform distribution of the platinum group metal on the support. For example, when the catalyst contains a high heat capacity, high mechanical strength alumina particulate support, a cationic platinum salt such as $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ is preferably used to impregnate the alumina. It has been observed that anionic salts such as platinum nitrate typically achieve a less uniform platinum distribution on the alumina particulate support.

Suitable reducible metal oxides for Catalyst A include the oxides of chromium, vanadium, molybdenum, cerium, praseodymium, neodymium, titanium, nickel, manganese, cobalt, as well as combinations thereof. Typically, there is at least 10 wt.% of the reducible metal oxide in the catalyst composition.

A preferred reducible metal oxide is cerium oxide. While cerium oxide alone as the reducible oxide component, in certain applications it is desired to include certain composite materials of cerium oxide. These cerium oxide composites additionally contain other rare earth metal oxides component such as oxides of lanthanum, praseodymium, and neodymium. In addition to these rare earth metal oxide composites, other composite materials such as zirconia-cerium oxide, gallium oxide-cerium oxide, titania-cerium oxide are also useful as a reducible metal oxide components in Catalyst A.

In both types of composite materials, it is believed that the additional component acts as a stabilizer for the cerium oxide component, although in some cases, the additional component may also serve to promote the water-gas shift reaction. In composites comprising cerium oxide with the additional components, the additional component may
5 comprise up to about 30 wt.% of the reducible metal oxide component of the composition.

Inorganic oxide supports for Catalyst A include high surface area refractory oxide supports. These refractory oxide supports include, for example, activated alumina, zirconia, titania, silica, zinc oxide and zeolites. These supports also include
10 combinations of these inorganic oxides such as stabilized forms of alumina including composites of zirconia, or silica with alumina, for example, alumina-zirconia, silica-alumina, and alumino-silicates.

In preferred embodiments of Catalyst A, the support is substantially comprised of alumina which preferably includes the members of the gamma or activated alumina
15 family, such as gamma and eta aluminas, and, if present, a minor amount of other refractory oxides, e.g., up to about 20 wt.% of silica, zirconia and titania. Preferably, the activated alumina has a specific surface area of at least 10 m²/g. More preferably, the activated alumina has a specific surface area of at least 150 m²/g.

In other preferred embodiments of Catalyst A, the catalyst supports possess high
20 heat capacity and high mechanical strength. Conventional, copper-based water-gas shift catalysts are prone to extremely rapid temperature rises upon exposure of the activated (reduced) catalysts to atmospheric air. The temperature rise is due to the rapid and exothermic oxidation of the reduced copper catalysts. Such rapid temperature rises can damage that catalyst due to sintering that occurs at high temperatures. In industrial
25 settings, reactors are equipped with sophisticated process controls and protocols that can control the temperature rise that occurs upon oxidation. In fuel cell processors in residential or vehicular applications, however, such controls and protocols are impractical to implement. The incorporation of copper-based catalysts that are less prone to the temperature rises in fuel cell processors is therefore desirable.

30 As described in copending United States Patent Application Serial No. 09/771,812, the pyrophoricity of copper-based water-gas shift catalyst having supports with high heat capacity and high mechanical strength, are lower as compared to conventional copper-based water-gas catalysts formed on catalyst supports of lower heat

capacity. The "low pyrophoricity" copper catalysts described in the application show comparable or improved catalytic activity to conventional copper based water-gas shift catalysts.

The low pyrophoricity catalysts in this embodiment include a structurally strong support of any suitable durable high heat capacity material, such as alumina, which is in a particulate form preferably having a longest dimension of about 1/32-inch (0.78 mm) to about 1/2 inch (1.25 cm) in cross section. Preferably, the support particle is at least 1/16-inch (1.56 mm) in cross section or, in other terms, has a mesh size of 12 (sieve opening of 1.52 mm) or above. For example, the support particle preferably has a mesh size of 12, 11, 10, etc. The catalytic supports in this embodiment are impregnated, with a suitable precursor of a reducible metal oxide, the copper catalytic agent and one or more platinum group metals. Preferred support materials have a heat capacity that is preferably higher than that of the reducible metal oxide. Examples of supports are silica, zeolites, zirconia, titania and alumina. Activated alumina is a particularly preferred support.

The high heat capacity particulate support in this preferred embodiment can take the form of any suitable high strength support such as a particle, pellet, extrudate, tablet and the like. The support is preferably in a durable, rigid form. A number of supports that are suitable for preparing the catalysts of the invention and practicing the methods of the invention are readily commercially available. For example, 1/8-inch diameter alumina particles available from ALCOA as DD-443 (with 327 m²/g BET surface area measured as received) can be used to practice the invention. Desirable characteristics for preferred supports include: having a high mechanical strength (resistance to crumbling), being readily available; having the capacity for being impregnated to high loadings with copper catalytic agents, reducible metal oxides and other catalyst additives; and possessing a high heat capacity. Supports with a heat capacity of at least the heat capacity of the reducible metal oxide are preferred. Supports with a heat capacity greater than the heat capacity of the reducible metal oxide are particularly preferred.

Due to their low pyrophoricity, high mechanical strength, high heat capacity particulate catalysts are preferred forms of Catalyst A. These catalysts can be prepared by first impregnating the particulate support with the reducible metal oxide precursor, followed by drying and calcination. For example, in a preferred preparation calcined 1/8-inch alumina support particles are impregnated in an aqueous solution of cerium

nitrate (or any other suitable CeO_2 precursor such as cerium acetate, chloride, etc.). The particles are then dried and calcined at 500°C in air to prepare the cerium oxide-impregnated alumina support (or “ CeO_2 /alumina particles”).

After preparation of the particulate support with the reducible metal oxide, the support can be impregnated with a precursor of the copper catalytic agent. The CeO_2 /alumina particles are impregnated with an aqueous solution of a water-soluble copper salt, e.g., copper (II) nitrate, at a weakly acidic pH. The particles are then dried and calcined to provide CuO/CeO_2 /alumina particles. Finally, the CuO/CeO_2 /alumina particles are similarly impregnated with a desired concentration of a water-soluble salt of the platinum group metal [e.g., $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$] followed by a calcination step to provide the CuO/CeO_2 /alumina particles impregnated with platinum.

In other embodiments of Catalyst A, wherein the catalyst is in the form of washcoat compositions, extrudates and tablets, the catalyst is preferably formed from powdered supports impregnated with the copper catalytic agent, the platinum group metal and reducible metal oxide.

The impregnated, powdered supports can be prepared by incipient wetness impregnation of the oxide support (e.g., activated alumina) with soluble salts of the reducible metal (e.g., cerium). For example, soluble salt forms of the reducible metal such as acetates, halides, nitrates, sulfates and the like can be utilized. This step is followed by drying and calcination steps to fix the reducible metal component as its oxide to the refractory oxide support.

The calcined support is then impregnated in analogous fashion with a desired concentration of a water-soluble salt of the copper (e.g., copper (II) nitrate) followed by drying and calcination steps. Finally, the resulting oxide support is impregnated with a desired concentration of a water-soluble salt of the platinum group metal (e.g., platinum nitrate) followed by a calcination step. The calcined, impregnated powdered oxide support containing the copper catalytic agent, the platinum group metal, and reducible metal oxide can then be formed into either an extrudate, tablet or washcoat composition for deposition on a monolith substrate.

In embodiments of the invention wherein the catalyst is in the form of extrudates, the calcined, powdered oxide support containing the copper catalytic agent, the platinum group metal, and reducible metal oxide is typically mixed with a binder and extruded

through a die of the desired shape. Typical useful binders include hydrated forms of alumina (e.g., pseudoboehmite), silica binders, clay binders, zirconia binders and the like.

Tablets can be prepared by: (1) combining the calcined, powdered oxide support with a binder; (2) shaping the combined powder and binder into the desired shape which could include tablets, pellets, beads, cylinders or hollow cylinders; and (3) calcining the shaped catalyst.

Washcoat compositions of the catalyst for deposition on monolith substrates (or "slurries") are prepared using methods known in the art. Preferably, the impregnated oxide support is ball milled as a suspension using sufficient water to prepare a slurry of a desired concentration. The concentration of the solids in the washcoat slurry can be used as a method to control the thickness of the catalyst coating ultimately deposited on the monolith substrate. For example, increasing the weight percentage of solids in the aqueous slurry will result in a thicker catalytic coat.

It is also generally advantageous to prepare slurries having particles of small particle sizes, e.g., less than 10 μm , to maximize the surface area of the catalyst upon deposition on the monolith substrate. Therefore, the particle size distribution of the slurry is typically measured, and milling is continued until the desired particle size has been achieved. Here again, binders are optionally included in the slurries to improve adherence of the washcoat to the monolith substrate walls.

The washcoat slurries are deposited on the monolith substrate by methods well-known to those of ordinary skill. Thus, for example, a layer of the supported copper catalyst can be prepared by dipping the substrate in a reservoir containing a sufficient volume of the slurry so that the substrate is fully immersed. The coated substrate can be subsequently dried and calcined.

As mentioned above, the washcoat catalyst compositions of the invention are disposed on monolith substrates to form coated monolith substrates. Although a variety of monolith substrates could be used, the monolith substrate is preferably of the type with one or more monolithic bodies having a plurality of finely divided gas flow passages (channels) extending there through. Preferably, the monolith substrate is of the type having a plurality of fine, parallel gas flow passages extending across the longitudinal axis of the substrate from an inlet or an outlet face, so that the channels are

open to fluid flow there through (often referred to as a "honeycomb substrate"). The passages, which are essentially straight from the inlet and outlet of the substrates, are defined by walls on which the catalyst composition can be coated in washcoat compositions so that the gases flowing through the passages contact the catalyst material.

5 Monolith substrates are commercially available in various sizes and configurations. The flow passages of the monolithic substrate are thin-walled channels which can be of any suitable cross-sectional shape and size such as trapezoidal, rectangular, square, sinusoidal, hexagonal, oval, circular. Such monolithic substrates may contain up to about 700 or more flow channels ("cells") per square inch of cross
10 section, although far fewer may be used. For example, the substrate can have from about 60 to 600, more usually from about 200 to 400, cells per square inch ("cps").

Various types of materials of construction for monolith substrates are known. The monolith substrate can be made from a variety of materials, including metal or ceramic monoliths. In some embodiments, the monolith substrate can be made from a
15 ceramic porous material composed of one or more metal oxides, e.g., alumina, alumina-silica, alumina-silica-titania, mullite, cordierite, zirconia, zirconia-ceria, zirconia-spinel, zirconia-mullite, silicon-carbide, and like. Some non-limiting examples of ceramic monoliths can include those made of: zirconium, barium titanate, porcelain, thorium oxide, magnesium oxide, steatite, boron or silicon carbonates, cordierite-alpha alumina,
20 silicon nitride, spodumene, alumina-silica magnesia, zircon silicate, sillimanite, magnesium silicates, zircon, petalite, alpha alumina and aluminosilicates. One example of a commercially available material for use as the substrate for the present invention is cordierite, which is an alumina-magnesia-silica material.

The metallic monolith substrate can be a honeycomb substrate made of a
25 refractory metal such as a stainless steel or other suitable iron based corrosion resistant alloys (e.g., iron-chromium alloy). Metal monoliths can be produced, for example, from alloys of chromium, aluminum and cobalt, such as those marketed under the trademark KANTHAL, or those produced from alloys of iron, chromium, aluminum and yttrium, marketed under the trademark of FECRALLOY. The metal can also be carbon steel or
30 simple cast iron. Monolith substrates are typically fabricated from such materials by placing a flat and a corrugated metal sheet one over the other and rolling the stacked sheets into a tubular configuration about an axis parallel to the configurations, to provide a cylindrical-shaped body having a plurality of fine, parallel gas flow passages, which

can range, typically, from about 200 to about 1,200 per square inch of face area. Heat exchangers, which are typically formed from metallic materials, can also be used as the monolith structures.

In other embodiments, the monolith substrate can be made of a ceramic or metal foam. Monolith substrates in the form of foams are well known in the prior art, e.g., see
5 US Patent 3,111,396 and SAE Technical Paper 971032, entitled "A New Catalyst Support Structure For Automotive Catalytic Converters" (February, 1997).

Catalyst B

10 Catalyst B contains a copper catalytic agent and one or more platinum group metals dispersed on a cerium oxide support. The catalyst can be in the form of extrudates, tablets, or washcoat compositions deposited on monolith substrates. Preferred forms of Catalyst B are as washcoat compositions deposited on monolith substrates.

15 Typically, there is at least 4 wt.% of copper in the Catalyst B composition. Preferably, there is about 4 to 12 wt.% of copper in Catalyst B. The copper is preferably dispersed on the inorganic oxide support by contacting the cerium oxide support with a water-soluble or water-dispersible salt of copper for sufficient time to impregnate the cerium oxide, followed by a drying step. The support material containing the copper can
20 then be calcined, preferably at a temperature above about 400 °C.

Catalyst B includes a platinum group metal, which is selected from the group consisting of platinum, palladium, rhodium, iridium and ruthenium. Preferably, the platinum group metal is platinum, palladium or rhodium, with platinum being particularly preferred. Analogous to the methods for preparation of Catalyst A, the
25 platinum group metals are typically dispersed on the cerium oxide support by impregnation followed by calcination. Preferably, the amount of the platinum group metal salts is chosen so that the final concentration of the platinum group metal on the support is about 0.1 wt.% to 2 wt.%, more preferably about 0.1 wt.% to 0.8 wt.%.

Cerium oxide serves as the support of Catalyst B. While cerium oxide alone can
30 be used for the support, in certain applications it may be desirable to include additives to the cerium oxide that stabilize the support. For example, certain composite materials of cerium oxide that additionally contain other rare earth metal oxides component such as

oxides of lanthanum, praseodymium, and neodymium are useful. In addition to these rare earth metal oxide composites, certain composite materials such as zirconia-cerium oxide, gallium oxide-cerium oxide, titania-cerium oxide are also useful as composite cerium-oxide support materials for Catalyst B. In both types of composite materials, it is
5 believed that the additional component acts as a stabilizer for the cerium oxide support, although in some cases, the additional component may also serve to promote the water-gas shift reaction. With composite support materials comprising cerium oxide with additional stabilizing component, typically the stabilizing component may comprise up to about 30 wt.% of the cerium oxide support of the composition.

10 Washcoat compositions, extrudates and tablets of Catalyst B are preferably formed from powdered cerium oxide impregnated with the copper catalytic agent and platinum group metal.

In a preferred embodiment, Catalyst B is prepared by impregnating cerium oxide powder with a solution of a water-soluble salt of copper, e.g., copper (II) nitrate,
15 followed by drying at, for example 120 °C, and calcination at, for example, 500 °C. Preferably, the impregnation is accomplished using incipient wetness impregnation wherein minimal volumes of copper salt solutions are employed to soak the cerium oxide support. The resulting cerium oxide support is then impregnated with a water-soluble salt of a platinum group metal, e.g., platinum nitrate. A drying and a calcination step
20 follow to provide powdered Catalyst B. The powdered Catalyst B composition can be formed into extrudates, tablets and washcoat compositions using the methods described above for forming the Catalyst A compositions.

As an alternative to the impregnation method described above, catalyst B can also be prepared by utilizing an aqueous solution containing a mixture of a water-soluble
25 cerium salt, e.g., cerium nitrate, and a water-soluble copper salt, e.g., copper (II) nitrate. The pH of the solution is then raised by addition of a base, e.g., sodium carbonate, to the solution to precipitate a material comprising a mixture of the corresponding hydroxides of copper and cerium. Preferably the solution is stirred during the precipitation step. The resulting coprecipitate is collected, dried and calcined to provide mixed metal oxide
30 material comprising copper oxide and cerium oxide. The mixed metal oxide material is then impregnated with an aqueous solution of a platinum group salt, dried and calcined to incorporate the platinum group metal component into the Catalyst B composition.

The invention also relates to processes for using the catalysts of the invention, i.e., Catalysts A and B. In a preferred embodiment the catalysts of the invention can be used in processes for producing hydrogen via the water-gas shift reaction. For example the catalyst of the invention can be incorporated in a reactor that is charged with an input
5 gas stream containing carbon monoxide and steam to produce hydrogen and carbon dioxide as products in the output gas stream.

The catalysts of the invention are reduced (activated) prior to their use in the water-gas shift reaction. The reduction can be effected using a reducing gas stream, preferably containing hydrogen, at 150 °C to 250 °C. Typically, the catalyst is heated to
10 a predetermined temperature and kept at that temperature, for a predetermined time, with the hydrogen-containing gas stream being passed therethrough. For operational simplicity and decreased startup time, it is preferred that the process gas itself, containing carbon monoxide, hydrogen and steam, serve as the reducing gas stream to activate the catalysts of the invention.

15 The composition of the input gas stream for the process can vary depending on the source of the reactant carbon monoxide. Although higher proportions of carbon monoxide can be accommodated in the process, the process of the invention is particularly effective wherein the carbon monoxide concentration is less than 10% by volume. Typically, molar excesses of steam are used relative to the amount of carbon
20 monoxide introduced into the input gas stream. Generally, H₂O:CO molar ratios of between 1:1 (i.e., "1.0") and 20:1 (i.e. "20.0") are preferred in the input gas stream, with higher ratios being particularly preferred for high conversion of carbon monoxide.

In fuel cell applications of the inventive process, input gas streams typically contain at least 10% by volume of hydrogen in addition to the carbon monoxide and
25 steam. Higher volumes, e.g., greater than 30-40% by volume, are often utilized in fuel cell applications.

In addition to carbon monoxide, steam and hydrogen, the input gas stream can contain carbon dioxide, nitrogen, and minor amounts of olefins, alcohols, aldehydes and/or other hydrocarbons. Preferably, the input gas stream contains not more than 4-5%
30 by volume of hydrocarbons and not more than 25% by volume carbon dioxide .

The reaction temperature of the water-gas shift process is dependent on the identity of the catalyst. For instance, processes conducted with water-gas shift Catalyst

A the reaction temperature is preferably below 350 °C, with temperatures of about 220-300 °C being particularly preferred. The optimal temperature ranges for Catalyst A make it an ideal candidate for incorporation into reactors serve as the “low-temperature” component in fuel processors. Catalyst A may be used, for example, in place of
5 conventional low temperature copper-zinc based catalysts such as $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ which typically operate at about 200 °C. It should be noted that lower temperatures could also be used, for example, when lower equilibrium carbon monoxide concentrations in the outlet gas stream are desired.

Where the water-gas shift process is conducted with Catalyst B, the reaction
10 temperature is preferably below 450 °C, with temperatures of about 350-400 °C being particularly preferred. For example, water-gas shift Catalyst B can be used to replace conventional high temperature iron-chromium based water-gas shift catalysts such as $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$ that typically operate at about 350 °C.

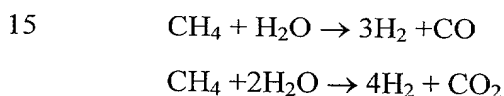
Reaction zone pressure is preferably maintained below the dew point pressure of
15 the reaction mixture. It should be recognized that lower or higher reaction zone pressures can be used such as from atmospheric up to about 500 psig.

Preferably, the water-gas shift reaction process is carried out in a continuous mode with the reactants being passed over the catalyst contained in one or more reaction zones. Gaseous hourly space velocities of about 500 to about 50,000 hr^{-1} VHSV
20 measured on the basis of dry gas under standard conditions are particularly suitable for most fuel cell operations. In embodiments wherein the catalysts are in the form of washcoat compositions deposited on monolith substrates, space velocities of up to 100,000 hr^{-1} VHSV may be possible. One skilled in the art would recognize that lower gas reactant flow rates favor more complete CO conversion.

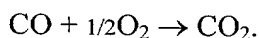
25 In certain embodiments of the process it may be preferable to include low concentrations of O_2 in the input gas stream as an additional measure to prevent the deactivation due to the presence of high concentrations of steam at lower temperatures. While not being bound by theory, Applicants believe that the oxidation of small portions of carbon monoxide serve to heat the catalyst and prevent catalyst deactivation.
30 Preferably less than 2% by volume oxygen is included in the input gas stream in this embodiment.

Although the water-gas shift catalysts and processes of the invention can be used in any application where hydrogen production is needed, a particularly useful application is in apparatus such as fuel processors that supply hydrogen to fuel cells. These systems typically comprise a series of reactors that convert hydrocarbon fuels (e.g., natural gas, gasoline, fuel oil, liquid petroleum gas, and the like) into hydrogen fuel. The conversions that take place in the reactors typically include reforming reactions and water gas shift reactions to produce hydrogen. Other reactors and trapping devices can also be included in the apparatus that reduce unwanted components in the hydrogen feed streams (e.g., carbon monoxide and sulfur components), that are ultimately supplied to the fuel cell.

As illustrated in the fuel processor (1) of Figure 1, the hydrocarbon reformer reactor (2) converts hydrocarbons (e.g., methane) and steam into hydrogen, carbon monoxide, and carbon dioxide. For example, methane is converted by the two reactions below:



The resulting gas is then reacted in the water-gas shift reactor (3) to further enrich the process gas in hydrogen, through the reaction of carbon monoxide with steam. Residual carbon monoxide in the process is then removed by selective carbon monoxide oxidation (with minimal hydrogen consumption) to carbon dioxide in the preferential oxidation reactor (4) according to the reaction:



The resulting process stream comprising high levels of hydrogen is then supplied to the fuel cell.

The following examples further illustrate the present invention, but of course, should not be construed as in any way limiting its scope.

Example 1: Preparation of Low-Pyrophoricity, Copper/Cerium Oxide/Platinum/Alumina Water-Gas Shift Catalysts (Exemplifies Preparation of High Mechanical Strength, High Heat Capacity Particulate Embodiments of Catalyst A)

To prepare a low-pyrophoricity catalyst wherein the support is alumina, the reducible metal oxide is ceria and the catalytic agent is CuO, ceria impregnated alumina support particles were prepared by incipient wetness impregnation of alumina beads or particulates.

5 1/8-inch alumina support particles (ALCOA DD-443) were dried for 2 hours at 200 °C and then calcined for 2 hours at 500 °C. The calcined 1/8-inch particles were then impregnated (i.e., impregnated at 55% incipient wetness to obtain about 15 wt.% CeO₂) in an aqueous solution of cerium nitrate (i.e., Ce(NO₃)₃, ; 33.44 g Ce(NO₃)₃ dissolved in 55 g water, per 100 g alumina). The particles were then dried at 120 °C for
10 8 hours. The sample was then calcined at 500 °C for 2 hours.

The ceria/alumina particles were subsequently impregnated (i.e., impregnated at 44% incipient wetness to obtain 8.25 wt.% CuO) with Cu-nitrate solution (i.e., 26.6 mL of 5M Cu(NO₃)₂ solution in 32 mL deionized water) at a pH of 6, dried at 120 °C for 8 hours and then calcined at 500 °C for 2 hours to prepare catalyst precursor particles
15 (CuO/ceria/alumina particles).

The CuO/ceria/alumina particles were then impregnated with Pt(NH₃)₄(NO₃)₂. 40 mg of Pt(NH₃)₄(NO₃)₂ in 35 mL per 100 g of catalyst precursor particles of water was used to prepare a catalyst containing 0.02 wt.% Pt. 200 ng of Pt(NH₃)₄(NO₃)₂ in 35 mL per 100 g of catalyst precursor particles of water was used to prepare a catalyst
20 containing 0.1 wt.% Pt. After impregnation, both catalysts were dried at 120 °C for 4 hours then calcined at 500 °C for 4 hours.

Example 2: Determination of Water-Gas Shift Catalyst Deactivation Rate at 250 °C

40 cc each of the 0.02 wt.% Pt- (Catalyst A1) and the 0.1 wt.% Pt-(Catalyst A2)
25 impregnated copper catalysts of Example 1 were evaluated along with a control catalyst (Catalyst C) prepared using the same procedure as described in Example 1 omitting the platinum impregnation step and the accompanying drying and calcining steps.

40 cc of each catalyst were loaded in 1 in diameter quartz reactor. A test gas composition containing 5.92% (v/v) of carbon monoxide, 7.40% CO₂, 31.82% H₂,
30 28.86% N₂ and 26% H₂O were passed over the catalyst at a flow rate of 1.5 L/min. The following temperature program for the catalyst was implemented:

(1) Heat the reactor to 200 °C and hold for 2 hours.

(2) Heat to 250 °C and hold for 2 hours.

(3) Cool to 100 °C and hold for five minutes.

The program was repeated continuously. A graphic representation of a single repeating unit of the temperature program is shown in Figure 2.

The activity of the catalyst is measured by the amount of CO converted to CO₂ in the gas stream at each segment at 200 °C and 250 °C. The concentration of CO in the output gas was detected using an infrared gas analyzer (California Analytical Instruments). The decline in activity of the catalyst over time is measured as the increase in CO concentration at 250 °C per minute of experiment time. A graphic representation of the decline in CO conversion (as measured by the outlet concentration of CO) over time as measured for catalysts A2 (+0.1 wt.% Pt) and C (0 wt.% Pt) are depicted in the graph in Figure 3. The data points observed Catalyst A2 are indicated by the triangles, and the data points observed with Catalyst C (the control catalyst) are indicated by diamonds. Best fit lines for the data points for the data point are also seen for Catalyst A2 and C. As can be seen in the graph, gradually higher CO concentrations are observed in the output gas stream over time for the control Catalyst C. The gradual increase in CO concentration in the output gas reflects the catalyst's instability to the high steam, low temperature conditions. In contrast, the decline in Catalyst A2's activity over time (observed as higher CO concentration in the output gas) is significantly less pronounced.

Table 1 summarizes the results of the experiment for all three catalysts.

Table 1

Catalyst Sample	Deactivation Rate @ 250 °C (ppm CO/min)	Initial Activity (% conversion)
Catalyst C (0 wt.% Pt)	2.03	82.5%
Catalyst A1 (0.02 wt.% Pt)	0.95	83.3%
Catalyst A2 (0.1 wt.% Pt)	0.37	85.0%

As can be seen in Table 1, the inclusion of the low concentration of platinum to the copper catalyst composition (Catalyst A1 and A2) has little significant impact on the initial activity of the catalyst. However, the rates at which the carbon monoxide conversion rate decline under these high-steam, low temperature conditions is

significantly different. The inclusion of as little as 0.02 wt.% Pt in the copper-based catalyst composition provides a catalyst whose deactivation rate is approximately half of the deactivation rate to the control catalyst (Catalyst C).

In summary, the graph shown in Figure 3 and the data in Table 1 demonstrate that the catalysts of the invention are significantly less prone to deactivation to high steam, low temperature conditions than other copper-based water-gas shift catalysts. The increased stability is observed without penalty to the water-gas shift catalyst's initial activity.

10 Example 3: Preparation of a Copper Ceria-supported Water-Gas Shift Reagent
Impregnated with 0.5 wt.% Pt (Exemplifies Preparation of Catalyst B)

205 g of cerium oxide powder (HSA-15 cerium oxide available from Rhodia, Inc.) was impregnated with 80.6 g of copper nitrate solution in water using the incipient wetness method. The powder was calcined using a two-step process; holding the
15 temperature at 120 °C for 2 hours, and then at 500 °C for 2 hours. The powder was cooled to yield an intermediate powder of 215 g cerium oxide impregnated with 8 wt.% copper oxide (CuO).

The intermediate powder was then impregnated with an aqueous solution of alkali-free amine-solubilized platinum hydroxide containing 1.08 g of platinum. After 1
20 hour, acetic acid was added to immobilize the platinum on the cerium oxide support. The resulting material was calcined using the two step procedure described above to yield cerium oxide support impregnated with 8 wt.% copper and 0.5 wt.% platinum.

A second portion of the intermediate cerium oxide powder (281 g) impregnated with 8 wt.% copper was prepared as described above. This portion was impregnated
25 with an aqueous solution of alkali-free amine-solubilized platinum hydroxide salt that contained 0.70 g of platinum, treated with acetic acid (15.15 g), and calcined using the two step calcination procedure to provide cerium oxide powder impregnated with 8 wt.% copper and 0.25 wt.% platinum.

3 in x 0.75 in 400 cpsi cordierite monolith pieces were coated with the two
30 slurries, dried and calcined; a dry gain of $\sim 2 \text{ g/in}^3$ was achieved.